

## LIQUID POLYMER COMPOSITION

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### Abstract of JP 6220157 (A)

**PURPOSE:** To obtain the subject composition, composed of a specific hydride, a specified reactive diluent, a specific plasticizer and a specified polyisocyanate compound, having a low viscosity, excellent in operating efficiency and heat resistance and useful as an electrical insulating material, a coating, material, etc.; **CONSTITUTION:** The objective composition is composed of (A) a hydrogenated hydroxyl group-containing liquid diene-based polymer in which >=60% conjugated diene-based monomer is bound through 1,4-bonds, (B) a reactive diluent composed of the hydrogenated hydroxyl group-containing liquid diene-based polymer in which >=60% 16-80C saturated dihydric alcohol and/or conjugated diene-based monomer is bound through 1,2-bonds, (C) a plasticizer such as a hydrogenated 1-decene oligomer in an amount of preferably 50-130 pts.wt. [based on 100 pts.wt. component (A)] and (D) a polyisocyanate compound such as tolylene diisocyanate. Furthermore, the content of hydroxyl groups in the component (B) is preferably 1-2.5 times expressed in terms of molar ratio based on that in the component (A). A cured product of this composition has <=50 JIS-A hardness.

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## (54) LIQUID POLYMER COMPOSITION

### (57)Abstract:

**PURPOSE:** To obtain the subject composition, composed of a specific hydride, a specified reactive diluent, a specific plasticizer and a specified polyisocyanate compound, having a low viscosity, excellent in operating efficiency and heat resistance and useful as an electrical insulating material, a coating, material, etc.

**CONSTITUTION:** The objective composition is composed of (A) a hydrogenated hydroxyl group-containing liquid diene-based polymer in which  $\geq 60\%$  conjugated diene-based monomer is bound through 1,4-bonds, (B) a reactive diluent composed of the hydrogenated hydroxyl group-containing liquid diene-based polymer in which  $\geq 60\%$  16-80C saturated dihydric alcohol and/or conjugated diene-based monomer is bound through 1,2-bonds, (C) a plasticizer such as a hydrogenated 1-decene oligomer in an amount of preferably 50-130 pts.wt. [based on 100 pts.wt. component (A)] and (D) a polyisocyanate compound such as tolylene diisocyanate. Furthermore, the content of hydroxyl groups in the component (B) is preferably 1-2.5 times expressed in terms of molar ratio based on that in the component (A). A cured product of this composition has  $\leq 50$  JIS-A hardness.

**\* NOTICES \***

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**CLAIMS**

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**[Claim(s)]**

[Claim 1]A hydride (A) of a hydroxyl group content liquefied diene system polymer in which not less than 60% of conjugated diene system monomers carried out 1 and 4-combination, A liquefied polymer composition in which a carbon number consists of reactive diluent (B), a plasticizer (C), and a polyisocyanate compound (D) which carried out 1 and 2-combination, and which consist of a hydride of a hydroxyl group content liquefied diene system polymer in saturated dihydric alcohol of 16-80, and/or not less than 60% of conjugated diene system monomers.

[Claim 2](A) The liquefied polymer composition according to claim 1 whose ingredients are a hydride of a hydroxyl group content liquefied isoprene polymer, and/or a hydride of a hydroxyl group content liquefied butadiene isoprene copolymer.

[Claim 3](A) The liquefied polymer composition according to claim 1 or 2 characterized by a hydroxyl group in the (B) ingredient being one to 2.5 times in a mole ratio to a hydroxyl group in an ingredient.

[Claim 4]A hardened material of the liquefied polymer composition according to claim 1 or 3 which has 50 or less JIS A hardness.

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[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Industrial Application] This invention is excellent in heat resistance and workability, relates to the liquefied polymer composition which gives the cured body of low hardness, and relates to the liquefied polymer composition which can be extensively used as an electric insulation material, a protective layer, a coating material, a paint, a water blocking material, etc.

#### [0002]

[Description of the Prior Art] The constituent which consists of combination of various hydroxyl group content liquefied diene system polymers and a polyisocyanate compound as a liquefied polymer composition for obtaining an elastic cured body etc. conventionally has been examined. As a liquefied polymer composition which gives the cured body excellent in a water resisting property, heat resistance, weatherability, an electrical property, etc. in these liquefied polymer compositions, The constituent which consists of the hydride and polyisocyanate compound of a hydroxyl group content liquefied isoprene system polymer is known (JP,63-57626,A, JP,1-203421,A). However, this constituent has high viscosity; and since it is a thing inferior to workability, it is important to choose and use a suitable viscosity-down agent.

[0003] Then, this invention persons as a liquefied polymer composition for obtaining the elastic cured body excellent in a water resisting property, heat resistance, weatherability, an electrical property, etc., The liquefied polymer composition which consists of the hydride of a hydroxyl group content isoprene system polymer, a polyisocyanate compound, and a hydride of oligomer of 1-decene is proposed (Japanese Patent Application No. No. 355549 [ three to ]). Thus, when the hydride of oligomer of 1-decene is used as a plasticizer, heat resistance improves and the viscosity down of a compound is also more possible for it than the case where other plasticizers are used. However, in order to obtain the cured body of the low hardness demanded for an electric insulation material use etc., the hydride of oligomer of a considerable amount of 1-decene needs to be added. For this reason, a problem arises in the heat resistance of the cured body obtained. Specifically the hardness change of the cured body after a heat test is dramatically large, or the problem of melting of a cured body arises, and a little more reliance is not obtained by heat resistance.

[0004] Then, as a result of inquiring wholeheartedly in order to obtain the liquefied polymer composition which canceled such a conventional fault, by using the reactive diluent which is a specific polyol compound, this invention persons find out that these problems are solvable, and came to complete this invention based on this knowledge.

#### [0005]

[Means for Solving the Problem]. Namely, as for this invention, not less than 60% of conjugated diene system monomers carried out 1 and 4-combination. . Saturated dihydric alcohol of 16-80 and/or not less than 60% of conjugated diene system monomers carried out [ a hydride (A) of a hydroxyl group content liquefied diene system polymer, and a carbon number ] 1 and 2-combination. A liquefied polymer composition which consists of reactive diluent (B), a plasticizer (C), and a polyisocyanate compound (D) which consist of a hydride of a hydroxyl group content liquefied diene system polymer, and its hardened material are provided.

[0006]In this invention, not less than 60% of conjugated diene system monomers use a hydride of a hydroxyl group content liquefied diene system polymer which carried out 1 and 4-combination as a (A) ingredient. . Not less than 60% of conjugated diene system monomers carried out 1 and 4-combination as a (A) ingredient here. Even if it uses not a hydride of a hydroxyl group content liquefied diene system polymer but a hydride of a hydroxyl group content liquefied diene system polymer in which not less than 60% of conjugated diene system monomers carried out 1 and 2-combination, for example, the purpose of this invention cannot be attained.

[0007]As a hydride of a hydroxyl group content liquefied diene system polymer used as a (A) ingredient in this invention, a number average molecular weight --- usually --- 300-25000 --- it is a thing of 500-10000 preferably --- hydroxyl group contents --- 0.1 - 10 meq/g --- it is a thing of 0.3 - 7 meq/g preferably. The sum total of \*\*\*- 1, four combination and the transformer 1, and four combination is not less than 70% of thing preferably not less than 60% in molecular structure. Although a hydroxyl group may be in any inside molecular chain terminals and a chain, its thing in especially molecular chain terminals is desirable. It is also possible to use together two or more sorts of hydroxyl group content liquefied diene system polymers, for example, a hydroxyl group content liquefied isoprene system polymer, and a hydroxyl group content liquefied isoprene butadiene copolymer in this invention.

[0008]Not less than 60% of the above conjugated diene system monomers a hydride of a hydroxyl group content liquefied diene system polymer which carried out 1 and 4-combination, A hydroxyl group content liquefied diene system polymer in which not less than 60% of conjugated diene system monomers carried out 1 and 4-combination can be obtained by hydrogenating using a publicly known method. Not less than 60% of conjugated diene system monomers can obtain as follows a hydroxyl group content liquefied diene system polymer which carried out 1 and 4-combination here, for example.

[0009]An azo compound which specifically has hydrogen peroxide and a hydroxyl group for one sort of diene monomers (specifically butadiene, isoprene, chloroprene, 1,3-pentadiene, a cyclopentadiene, etc.) of the carbon numbers 4-22, or two sorts or more (for example, 2 and 2'-azobis) [2-methyl-N-(2-hydroxyethyl) propionamide] etc. Or by making into a polymerization initiator peroxide (for example, cyclohexanon peroxide etc.) which has a hydroxyl group, and carrying out a radical polymerization, Hydroxyl group content liquefied diene system polymers (for example, hydroxyl group content liquefied polyisoprene, a hydroxyl group content liquefied isoprene butadiene copolymer, etc.) are obtained. As a hydroxyl group content liquefied diene system polymer, when manufacturing an isoprene butadiene copolymer, a copolymerization ratio can be changed with a charge of a diene monomer at the time of a polymerization in [ arbitrary ] isoprene/butadiene =30 / 70 - 95/5 (wt/wt).

[0010]The amount of polymerization initiator used in this case is 1.0-g [ 50 ], 2, and 2'-azobis, when using hydrogen peroxide as opposed to 100 g of diene monomers. When using [2-methyl-N-(2-hydroxyethyl) propionamide] and using 5.0-100g, and cyclohexanon peroxide, 5.0-100g are suitable. Although it is also possible to perform a polymerization with a non-solvent, it is preferred to use a solvent for an ease of control of a reaction, etc. As a solvent, ethanol, isopropanol, n-butanol, etc. are usually used. 0.5 to 15 hours of reaction temperature are suitable for 80-150 \*\* and reaction time.

[0011]At the time of a polymerization, two or more sorts of diene monomers can also be mixed and used. To a diene monomer, at a rate below 50 mol % An addition condensation nature monomer of the carbon numbers 2-22. (For example, a butene, a pentene, styrene, alpha-methylstyrene, acrylonitrile, acrylic acid and its ester, methacrylic acid and its ester, VCM/PVC, vinyl acetate, acrylamide, etc.) can also be added.

[0012]If it distills under decompression of a solution after ending reaction, a hydroxyl group content liquefied diene system polymer in which a solvent, an unreacted monomer, etc. were removed and not less than 60% of conjugated diene system monomers carried out 1 and 4-combination will be obtained. Carry out anionic polymerization of the diene monomer here using catalysts, such as for example, naphthalene dilithium, and an isoprene living polymer or an isoprene butadiene copolymerization living polymer is manufactured, When a mono epoxy compound etc. are made to react furthermore, not less than 60% of conjugated diene system

monomers will be the hydroxyl group content liquefied diene system polymers which carried out 1 and 2-combination.

[0013]The (A) ingredient in this invention can obtain a hydroxyl group content [ in which not less than 60% of conjugated diene system monomers carried out 1 and 4-combination ] liquefied diene polymer manufactured like the above by hydrogenating with a publicly known technique using a homogeneous catalyst and a heterogeneous catalyst.

[0014]When using a homogeneous catalyst first, aromatic hydrocarbon, such as saturated hydrocarbon and benzene, such as hexane and cyclohexane, toluene, and xylene, is used as a solvent, and a hydrogenation reaction is performed under ordinary pressure – hydrogen pressure of 50kg/cm<sup>2</sup>G at ordinary temperature –150 \*\* reaction temperature. As a homogeneous catalyst, 0.01–0.1 mol % grade use of the Ziegler catalyst by combination of transition metal halide and alkylation things, such as aluminum, alkaline–earth metals, or an alkaline metal, etc. per double bond of polymer is carried out. A reaction is usually ended in 1 to 24 hours.

[0015]On the other hand, in using a heterogeneous catalyst etc., saturated hydrocarbon, such as hexane and cyclohexane, Aromatic hydrocarbon, such as benzene, toluene, and xylene, diethylether, and a tetrahydrofuran (THF), At ordinary temperature –200 \*\* reaction temperature, a hydrogenation reaction is performed under ordinary pressure – hydrogen pressure of 100 kg/cm<sup>2</sup>G, using such mixed stock, such as alcohols, such as ether, such as dioxane, ethanol, isopropanol, and 1-butanol, as a solvent. What is necessary is to be independent, or to support catalysts, such as nickel, cobalt, palladium, platinum, rhodium, and a ruthenium, to carriers, such as silica, diatomite, alumina, and activated carbon, and just to use them as a heterogeneous catalyst. 0.05 to 10 % of the weight is suitable for the amount of catalyst used to polymer weight. These catalysts may mix and use two or more sorts. A reaction is usually ended in 1 to 48 hours.

[0016]If a \*\* exception carries out a catalyst after ending reaction and a solution is distilled under decompression, a hydride of a hydroxyl group content liquefied diene system polymer in which not less than 60% of conjugated diene system monomers carried out 1 and 4-combination which a solvent is removed and is made into the purpose will be obtained. Thus, 300–25000, and thing of a number average molecular weight that are 500–10000 preferably and whose hydroxyl group contents are 0.1 – 10 meq/g are [ a hydride of a hydroxyl group content liquefied diene system polymer obtained ] desirable.

[0017]As for a hydrogenation rate of a hydride of the above-mentioned hydroxyl group content liquefied diene system polymer, it is preferred that it is not less than 50%, and it is preferred that it is especially not less than 70%. In this invention, a mixture of a hydride of a hydroxyl group content liquefied isoprene system polymer and a hydride of a hydroxyl group content liquefied isoprene butadiene copolymer can also be used, for example. A rate of hydrogenation of an unsaturated double bond in a polymer after a hydrogenation rate, i.e., a hydrogenation reaction, is expressed with a lower type here.

[0018]

[Equation 1]

$$\text{水素化率} = \frac{\text{水素化前の重合体の臭素価} - \text{水素化後の重合体の臭素価}}{\text{水素化前の重合体の臭素価}} \times 100$$

[0019]As for especially the number of average hydroxyl groups per molecule, in this invention, it is preferred as a hydride of a hydroxyl group content liquefied diene system polymer to use what is 2.0 or more 1.7 or more from a viewpoint of obtaining the cured body of good physical properties. The number of average hydroxyl groups per molecule is expressed with the following formula.

[0020]

[Equation 2]

$$\text{一分子当たりの平均水酸基数} = \frac{\text{水酸基数含量 (meq/g)}}{1000} \times \text{数平均分子量}$$

[0021]Next, in this invention, reactive diluent is used as a (B) ingredient. The reactive diluent used by this invention here is the hydride of a hydroxyl group content liquefied diene system polymer in which saturated dihydric alcohol of the carbon numbers 16–80 and/or not less than 60% of conjugated diene monomers carried out 1 and 2-combination.

[0022]The dimer diol produced by returning dimer acid ester as saturated dihydric alcohol of the carbon numbers 16–80 here can be mentioned as the example. Dimer diol is the long chain glycol of a straight chain or branched chain, and what has a cyclo ring in intramolecular may be contained in these.

[0023]The dimer diol specifically produced as such dimer diol by returning the dimethyl ester of the dimer acid (the Henkel Hakusui make, a trade name; purser dime 288) of the carbon number 36 is mentioned. The long chain dibasic acid of the carbon number 22 (the product made from Okamura Oil Mill, trade name;IPS-22, IPU-22, etc.), The long chain glycol produced by returning dimethyl ester, such as long chain dibasic acid (the product made from Okamura Oil Mill, trade name;SL-20, UL-20, SB-20, UB-20, etc.) of the carbon number 20 and long chain dibasic acid (the product made from Okamura Oil Mill, trade name;ST-2P) of the carbon number 28, is mentioned. The hydrogenation things (the Arakawa Chemical Industries, Ltd. make, a trade name; dimer diol KX-501 etc.) of the long chain dibasic acid of the carbon numbers 36 and 72 are mentioned.

[0024]Although dimer acid is a mixture which shows polymer fatty acid usually produced by polymerizing unsaturation aliphatic monocarboxylic acid, such as linolic acid and oleic acid, and generally consists of an unreacted monomer and other high order polymers besides a dimer of the main ingredients, Dimer acid which high-concentration-ized a dimer may be used by vacuum distillation etc. if needed.

[0025]As a hydride of a hydroxyl group content liquefied diene system polymer which makes another side of the (B) ingredient and in which not less than 60% of conjugated diene monomers carried out 1,2-combination, a hydride of hydroxyl group content 1,2-polybutadiene can be illustrated. A hydride of this hydroxyl group content 1,2-polybutadiene can be obtained by hydrogenating hydroxyl group content 1,2-polybutadiene. Specifically, trade name;NISSOPB GI-1000 by Nippon Soda Co., Ltd., trade name; polytail HA by Mitsubishi Kasei Corp., etc. are mentioned as a hydride of such hydroxyl group content 1,2-polybutadiene. A content of a 1,2-vinyl group of a hydride of such hydroxyl group content 1,2-polybutadienes is a thing beyond 60 mol %.

[0026]In this invention, a hydride of a hydroxyl group content liquefied diene system polymer in which not less than 60% of conjugated diene monomers considered 1 and 2-combination as the above-mentioned saturated dihydric alcohol is independently used as a (B) ingredient, respectively, or both compounds are used together. As an addition of such reactive diluent (B), A ratio of the number of mols of a hydroxyl group of a hydride of a hydroxyl group content liquefied diene system polymer (a) to the number of mols of a hydroxyl group in reactive diluent (b) so that it may become the range of (b)/(a) = 1.0 – 2.5, That is, it is preferred to use to a hydroxyl group in the (A) ingredient, so that a hydroxyl group in the (B) ingredient may be one to 2.5 times in a mole ratio. If a mole ratio is too large, hardness of a hardened material obtained becomes large and is not preferred.

[0027]In this invention, a plasticizer is used as a (C) ingredient. As for a \*\*\*\*\* [ here ] plasticizer, although it is usable also in what is generally used fundamentally, it is preferred oligomer of alpha olefin of a heat-resistant point to the carbon numbers 8–14 and to use a hydride of 1-decene oligomer especially.

[0028]With a hydride of 1-decene oligomer, a residual double bond of oligomer which polymerized 1-decene using organic peroxide, a coordination anion catalyst, the Friedel crafts type catalyst, etc. is hydrogenated here, and it is often sold by a name called the Polly alpha olefin (PAO). Although there is no restriction in particular as a catalyst used in the case of this polymerization, the Friedel crafts type catalysts, such as boron trifluoride and  $\text{AlCl}_3$ , are used comparatively.

Hydrogenation can be easily performed using a catalyst of a Raney nickel catalyst, stabilization

nickel, etc.

[0029]A hydride of such 1-decene oligomer has that preferred whose kinetic viscosity at 40 \*\* is 45 – 100cst. When good heat resistance [ in / at a thing of less than 45 cst / in kinetic viscosity / an elevated temperature ] is not obtained but kinetic viscosity exceeds 100cst on the other hand here, it becomes difficult to obtain a liquefied polymer composition of hypoviscosity, and it is inferior to workability.

[0030]When using a hydride of 1-decene oligomer as a (C) ingredient, the addition is 50 – 130 weight section preferably 30 to 200 weight section to hydride 100 weight section of a hydroxyl group liquefied diene system polymer which is the aforementioned (A) ingredient.

[0031]A hydride of 1-decene oligomer used by this invention has that preferred whose total content of a tetramer, a pentamer, and a hexamer is 75 % of the weight or more. Even if a total content of a tetramer, a pentamer, and a hexamer goes into the range of the above [ kinetic viscosity ] by less than 75% of the weight of a thing here, good heat resistance may not be obtained. Content of a tetramer, a pentamer, and a hexamer can be determined by a gas chromatograph etc.

[0032]As 1-decene oligomer marketed, Idemitsu PAO 5002,5004,5006,5008, 5010 (product made from Idemitsu Petrochemistry), IH-30, IH-47, IH-63 (made by an ethyl company), PAO 40, PAO 100 (made by a uni-royal company), etc. are mentioned.

[0033]As other plasticizers, it is paraffin series process oil. [For example, trade name ;P W-90] (made by Idemitsu Kosan) \*\*, ethylene-alpha olefin system co-oligomer [Trade name; roux cant HC-20 [ for example, ] (product made from Mitsui Petrochemistry)] A thing of a \*\* silicone series can be used.

[0034]Next, in this invention, a polyisocyanate compound is used as a (D) ingredient. A polyisocyanate compound is an organic compound which has two pieces or an isocyanate group beyond it in one molecule here, It has an isocyanate group which carries out reactivity to a hydroxyl group in reactive diluent which is a hydride of a hydroxyl group content liquefied diene system polymer and the (B) ingredient which are the aforementioned (A) ingredients. As an example of this polyisocyanate compound, a thing of the usual aromatic series, aliphatic series, and alicycle fellows can be mentioned.

[0035]Specifically For example, tolylene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), Carbodiimide denaturation diphenylmethane diisocyanate, a polymethylene polyphenyl isocyanate, Phenylene diisocyanate, the naphthalene 1, 5-diisocyanate, Aromatic polyisocyanates, such as o-toluidine diisocyanate, triphenylmethane triisocyanate, tris(isocyanatephenyl) thio phosphate, the isopropyl benzene 2, and 4-diisocyanate, can be mentioned.

[0036]Aliphatic series-aromatic polyisocyanates, such as xylylene diisocyanate (XDI) and tetramethyl xylylene diisocyanate (TMXDI) (an isocyanate group) That is [ it does not have the isocyanate group coupled directly with an aromatic ring via aliphatic hydrocarbon ], polyisocyanate which does not have the isocyanate group coupled directly with an aromatic ring can be mentioned into a molecule.

[0037]Hexamethylene di-isocyanate, dodecane diisocyanate, Lysine diisocyanate, lysine ester tri-isocyanate, 1,6,11-undecane-tri-iso-isocyanate, Aliphatic series polyisocyanates, such as 1,8-diisocyanate 4-isocyanatemethyloctane, 1,3,6-hexamethylene tri-isocyanate, and trimethyl hexamethylene di-isocyanate, can be mentioned.

[0038]Transformer cyclohexane-1,4-diisocyanate, bicycloheptane tri-isocyanate, Isophorone diisocyanate (IPDI), dicyclohexylmethane diisocyanate (hydrogenation MDI), Alicycle fellows polyisocyanates, such as hydrogenation tolylene diisocyanate, hydrogenation xylylene diisocyanate, and hydrogenation tetramethyl xylylene diisocyanate, can be mentioned.

[0039]in addition, cyclization of said polyisocyanate compound -- a trimer (isocyanurate denaturation object). A view let denaturation object, ethylene glycol, 1,4-butanediol, Propylene glycol, dipropylene glycol, trimethylolpropane, Polyether polyol, polymeric polyol, polytetramethylene ether glycol, An addition reaction thing of polyol compounds, such as a hydride of polyester polyol, acrylic polyol, poly alkadiene polyol, and poly alkadiene polyol, a partial saponification ethylene-vinylacetate copolymer, and castor oil system polyol, and said polyisocyanate compound, etc. are used.

[0040]These polyisocyanate compounds can mix two or more sorts, and can also be used, Furthermore, an isocyanate group of these polyisocyanate compounds Phenols, What is called a block isocyanate compound blocked by blocking agents, such as oxime, imide, mercaptans, alcohols, epsilon caprolactam, ethyleneimine, alpha-pyrrolidone, diethyl malonate, sodium hydrogen sulfite, and boric acid, can also be used.

[0041]Reactive diluent which usually has a hydroxyl group (OH) of a hydride of a hydroxyl group content liquefied diene system polymer which is the aforementioned (A) ingredient, and a hydroxyl group reacted to an isocyanate group although there is no restriction in particular about a blending ratio of these polyisocyanate compounds [(B) Ingredient] an isocyanate group (NCO) of a polyisocyanate compound to the sum total of an inner hydroxyl group -- comparatively (NCO/OH) -- a mole ratio -- final -- 0.3-5 -- it blends so that it may be preferably set to 0.5-2.5 eventually.

[0042]Here, the word "last target" is used because various methods are used in production of a actual cured body. It divides roughly and a one-shot process, the prepolymer method (1), and three sorts of methods of (2) are mentioned. A one-shot process blends an ingredient except a polyisocyanate compound at least among all the combination ingredients first, is mixed, and obtains a mixture. A combination drug ingredient which was not used for this mixture by mixing of a polyisocyanate compound and the point is added, it mixes, and a liquefied polymer composition is obtained. Desirable NCO/OH at this time is 0.5-2.5.

[0043]Ranges of predetermined equivalent ratio NCO/OH of the prepolymer method (1) are 1.7-25, At least 1 of compounds (a hydride of a hydroxyl group content liquefied diene system polymer and reactive diluent) which have a hydroxyl group, and a polyisocyanate compound are made to react under existence of some or all of other additive agents, or nonexistence, and a prepolymer is obtained. Desirable NCO/OH at this time is 0.5-2.5. In this case, since mole-ratio NCO/OH of a functional group which participated in a reaction is 1.0 substantially when a prepolymer is obtained, final NCO/OH is within the limits of 0.5-2.5 preferably.

[0044]Next, ranges of predetermined equivalent ratio NCO/OH are 1.7-5, and the prepolymer method (2) blends all the combination ingredients, makes them react, and obtains a prepolymer. This prepolymer is made to react to humidity (water) in the air. Also in this case, final NCO/OH is within the limits of 0.5-2.5 preferably. As mentioned above, although various methods are used in production of a actual cured body, final NCO/OH is within the limits of 0.5-2.5 preferably.

[0045]In this invention, as mentioned above, although a hydride (A), reactive diluent (B), a plasticizer (C), and a polyisocyanate compound of a hydroxyl group content liquefied diene system polymer are used as a fundamental ingredient, In order to raise the mechanical properties of a liquefied polymer composition further, according to the purpose, other ingredients can be added in the range which does not spoil main point of this invention.

[0046]In this invention, in order to promote a reaction, various catalysts can be added. Specifically For example, triethylenediamine, tetramethyl guanidine, N,N,N'N'- tetramethyl hexane-1,6-diamine and N,N,N' N"N"-pentamethyl diethylenetriamine, Bis(2-dimethylaminoethyl) ether, 1,2-dimethylimidazole, Carboxylate of the third class amine, such as an N-methyl-N'-(2-dimethylamino) ethylpiperazine and diazabicycloundecen, or this the third class amine, Furthermore, stannous octoate, Djibouti rutin diacetate, dibutyltin dilaurate, Organic metallic compounds, such as Djibouti rutin marker PUCHIDO, Djibouti rutin thiocarboxylate, dibutyltin dimaleate, dioctyl Zschimmer KAPUCHIDO, dioctyltin thiocarboxylate, phenyl mercury propionate, and lead octenate, can be added. Additions of these catalysts are a maximum of 10 weight sections to hydride 100 weight section of a hydroxyl group content liquefied diene system polymer which is the aforementioned (A) ingredient. When an addition of a catalyst exceeds ten weight sections, since a hardening facilitatory effect is not only reaching the ceiling, but the danger of a local anomalous reaction (gelling) becomes large, it is not desirable.

[0047]In this invention, inorganic matter and an organic bulking agent other than an ingredient which participates in a reaction directly as mentioned above can be added if needed. As an inorganic filler which can be used in this invention, Zinc, aluminum, copper, nickel, a glass bulb, a glass flake, glass fiber, carbon black (channel black, furnace black, and acetylene black.) Thermal black, carbon fiber, graphite, asbestos, kaolin clay, Agalmatolite clay, talc, nepheline, the Cryo

light, cay welded pyroclastic rock, diatomite, Slate powder, whiting, feldspar powder, mica, gypsum, quartz powder, Fines silicic acid, attapulgite, a sericite, volcanic ash, a vermiculite, silica, Alumina, a zinc oxide, magnesium oxide, zirconium oxide, titanium oxide, Iron oxide, a molybdenum dioxide, aluminium hydroxide, magnesium hydroxide, calcium carbonate, magnesium carbonate, barium sulfate, a calcium silicate, zeolite, potassium titanate, boron nitride, a boron night light, molybdenum disulfide, etc. can be mentioned.

[0048]As an organic filler which can be used in this invention, Textiles of natural systems, such as a rubber crumb, cellulose, lignin, a chitinous substance, leather powder, coconut husks, wood flour and cotton, hemp, wool, and silk, Synthetic fibers, such as nylon, polyester, vinylon, acetate, and an acrylic, Synthetic resin powder or granulation, such as polyethylene, polypropylene, polystyrene, ABS plastics, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polymethylmethacrylate, vinyl chloride resin, an epoxy resin, and phenol resin, etc. can be mentioned. Although there is no restriction in particular about loadings of these inorganic fillers and an organic filler, it is usually 5 – 200 weight section preferably 0.5 to 500 weight section to hydride 100 weight section of a hydroxyl group content liquefied diene system polymer which is the aforementioned (A) ingredient.

[0049]In this invention, adhesive grant resin, an antiaging agent (an antioxidant, an ultraviolet ray absorbent), fire retardant, a defoaming agent, an antifoaming agent, etc. can be added as other additive agents at a stage of either under [ before a reaction ] reaction or an after [ a reaction ] if needed.

[0050]That is, adhesive grant resin can be used for adjustment of adhesive power and adhesive strength. Specifically, there are alkylphenol resin, terpene resin, terpene phenol resin, xylene formaldehyde resins, rosin, hydrogenation rosin, coumarone resin, aliphatic series, alicycle fellows, aromatic petroleum resin, etc.

[0051]Antiaging agents (an antioxidant, an ultraviolet ray absorbent), such as a hindered phenol system, a hindered amine system, and a benzotriazol system, can be added for heat resistance and weatherproof improvement.

[0052]Fire retardant, such as phosphorus compounds, a halogenated compound, and antimony oxide, can be blended, defoaming agents, such as a silicone compound, can be blended, or antifoaming agents, such as zeolite and quicklime, etc. can also be blended.

[0053]Although a liquefied polymer composition of this invention is obtained by mixing the above-mentioned ingredient, by following methods, this constituent can be stiffened and can generally be used as a cured body. First, as described above, a predetermined ingredient is blended at a predetermined rate and a liquefied polymer composition is prepared. If in charge of preparation of a constituent, using a mixed device, a kneading apparatus, etc., it is 15–100 \*\* in temperature preferably, and 0–120 \*\* carries out stirring mixing preferably for – 5 hours during 1 second for for 0.5 second to 8 hours. Usually, a method called the \*\*\*\* one-shot process or a method called the prepolymer method is used for preparation of a constituent.

[0054]In a one-shot process, an ingredient except a polyisocyanate compound is first blended at least among said ingredients, it mixes in the above-mentioned temperature and time, and a mixture is obtained. An additive component which was not used for this mixture by mixing of a polyisocyanate compound and the point is added, it mixes in the above-mentioned temperature and time, and a liquefied polymer composition is obtained. Desirable NCO/OH at this time is 0.5–2.5.

[0055]The prepolymer method (1) of the prepolymer methods, In 1.7–25, predetermined equivalent ratio NCO/OH makes at least 1 of a hydride of a hydroxyl group content liquefied diene system polymer, and reactive diluent, and a polyisocyanate compound react under existence of some or all of other additive agents, or nonexistence, and obtains a prepolymer. Temperature of a reaction is the same as that of the above, and reaction time is usually 0.5 to 8 hours preferably for 0.1 to 10 hours. The remaining ingredients are mixed in the above-mentioned temperature and time to this prepolymer, and a liquefied polymer composition is obtained. Desirable NCO/OH at this time is 0.5–2.5.

[0056]Predetermined equivalent ratio NCO/OH blends all the combination ingredients, makes them react in 1.7–5, and the prepolymer method (2) obtains a prepolymer. Temperature of a

reaction is the same as that of the above, and reaction time is usually 0.5 to 8 hours preferably for 0.1 to 10 hours. This prepolymer is made to react to humidity (water) in the air. Thus, by carrying out curing treatment with a conventional method, the prepared liquefied diene system polymer composition can give a cured body of various gestalten, and various kinds of uses are presented with it. Hardness of a cured body produced by doing in this way is 50 or less JIS A in general, and is excellent in workability.

[0057]

[Example]Next, an example explains this invention in detail.

200 g of isoprene, the hydrogen peroxide solution 40g of 20% of concentration, and 100 g of isopropanol were taught to the resisting pressure reaction vessel made from stainless steel of the preparation 1 liter capacity of example of manufacture 1(1) hydroxyl-group end liquefied polyisoprene, and it reacted to it on the temperature of 120 \*\*, and the conditions of reaction-time 2 hours. During the reaction, the pressure reached at a maximum of 8 kg/cm<sup>2</sup>G. The oil reservoir was isolated preparatively after having put the reaction mixture into the separating funnel, having added and shaken 600 g of water, after the reaction was completed, and settling for 3 hours. A solvent, a monomer, and low boiling point components were distilled off on 2mmHg, 100 \*\*, and the conditions of 2 hours, and the liquefied polyisoprene (66 % of the weight of yield) which has a hydroxyl group in molecular chain terminals was obtained from this oil reservoir. The number average molecular weight of this thing was 2240, and, as for 0.96 meq/g and viscosity, 64 poise/30 \*\*, and the bromine number of hydroxyl group contents were 220g/100g. The number of average hydroxyl groups per molecule at this time is 2.15. In \*\*\*\*- 1 and four combination, 1 and 2 combination was [ the transformer 1 and four combination / four combination of the structural analysis result by <sup>1</sup>H-NMR ] 4% 6%3 33% 57%.

[0058](2). Obtained by carrying out like the preparation above (1) of the hydride of hydroxyl group end liquefied polyisoprene. The cyclohexane 100g was taught to molecular chain terminals as 100 g of liquefied polyisoprene which has a hydroxyl group, 5g of ruthenium carbon catalysts of 5 % of the weight of ruthenium contents, and a solvent, and the hydrogenation reaction was performed at 150 \*\* under the hydrogen pressure of 50 kg/cm<sup>2</sup>G for 6 hours. After letting a 0.45-micrometer membrane filter pass after ending reaction and carrying out separation removal of the catalyst from a reaction solution, the solvent was distilled off on 2mmHg, 110 \*\*, and the conditions of 2 hours. As a result, the hydride of the liquefied polyisoprene which has a hydroxyl group in molecular chain terminals was obtained. The number average molecular weight of this thing was 2310, and 0.94 meq/g, the viscosity of 625 poise/30 \*\*, and the bromine number of hydroxyl group contents were 2g/100g. The number of average hydroxyl groups per molecule at this time is 2.17.

[0059]200 g of isoprene, the hydrogen peroxide solution 100g of 30% of concentration, and 300 g of isopropanol were taught to the resisting pressure reaction vessel made from stainless steel of the preparation 1 liter capacity of example of manufacture 2(1) hydroxyl-group end liquefied polyisoprene, and it reacted to it on the temperature of 115 \*\*, and the conditions of reaction-time 2.5 hours. During the reaction, the pressure reached at a maximum of 7 kg/cm<sup>2</sup>G. The oil reservoir was isolated preparatively after having put the reaction mixture into the separating funnel, having added and shaken 600 g of water, after the reaction was completed, and settling for 3 hours. A solvent, a monomer, and low boiling point components were distilled off on 2mmHg, 100 \*\*, and the conditions of 2 hours, and the liquefied polyisoprene (71 % of the weight of yield) which has a hydroxyl group in molecular chain terminals was obtained from this oil reservoir. The number average molecular weight of this thing is 1380, and is hydroxyl group contents. 1.55 meq/g and viscosity were 46 poise/30 \*\*. The number of average hydroxyl groups per molecule at this time was 2.14. In \*\*\*\*- 1 and 4-combination, 1 and 2 combination was [ the transformer 1 and 4-combination / four combination of the structural analysis result by <sup>1</sup>H-NMR ] 5% 6%3 33% 56%.

[0060](2). Obtained by carrying out like the preparation above (1) of the hydride of hydroxyl group end liquefied polyisoprene. The cyclohexane 100g was taught to molecular chain terminals

as 100 g of liquefied polyisoprene and 5g of ruthenium carbon catalysts of 5 % of the weight of ruthenium contents which have a hydroxyl group, and a solvent, and the hydrogenation reaction was performed at 150 \*\* under the hydrogen pressure of 50 kg/cm<sup>2</sup>G for 6 hours. After letting a 0.45-micrometer membrane filter pass after ending reaction and carrying out separation removal of the catalyst from a reaction solution, the solvent was distilled off on 2mmHg, 110 \*\*, and the conditions of 2 hours. As a result, the hydride of the liquefied polyisoprene which has a hydroxyl group in molecular chain terminals was obtained. The number average molecular weight of this thing was 1420, and, as for 1.54 meq/g and viscosity, 298 poise/30 \*\*, and the bromine number of hydroxyl group contents were 1g/100g. The number of average hydroxyl groups per molecule at this time is 2.19.

[0061]To the resisting pressure reaction vessel made from stainless steel of the preparation 1 liter capacity of an example of manufacture 3(1) hydroxyl-group content liquefied isoprene butadiene copolymer. 90 g of isoprene, the butadiene 110g, the hydrogen peroxide solution 40g of 20% of concentration, and 100 g of isopropanol were taught, and it reacted on the temperature of 120 \*\*, and the conditions of reaction-time 2 hours. During the reaction, the pressure reached at a maximum of 8 kg/cm<sup>2</sup>G. The oil reservoir was isolated preparatively after having put the reaction mixture into the separating funnel, having added and shaken 600 g of water, after the reaction was completed, and settling for 3 hours. A solvent, a monomer, and low boiling point components were distilled off on 2mmHg, 100 \*\*, and the conditions of 2 hours, and the hydroxyl group content liquefied isoprene butadiene copolymer (62 % of the weight of yield) was obtained from this oil reservoir. The number average molecular weight of this thing was 2240, and, as for 0.91 meq/g and viscosity, 44 poise/30 \*\*, and the bromine number of hydroxyl group contents were 215g/100g. The number of average hydroxyl groups per molecule at this time is 2.04. The structural analysis result by <sup>1</sup>H-NMR is 45% of an isoprene content.

It was 55% of a butadiene content.

In 1 and 4-combination, 1 and 2-combination was [ 4-combination ] 2% 14%3 84%.

[0062](2) The hydroxyl group end liquefied isoprene butadiene copolymer 100g which obtained by carrying out like the preparation above (1) of the hydride of a hydroxyl group end liquefied isoprene butadiene copolymer, The cyclohexane 100g was prepared as 5g of ruthenium carbon catalysts of 5 % of the weight of ruthenium contents, and a solvent, and the hydrogenation reaction was performed at 150 \*\* under the hydrogen pressure of 50 kg/cm<sup>2</sup>G for 6 hours. After letting a 0.45-micrometer membrane filter pass after ending reaction and carrying out separation removal of the catalyst from a reaction solution, the solvent was distilled off on 2mmHg, 110 \*\*, and the conditions of 2 hours. As a result, the hydride of the liquefied isoprene butadiene copolymer which has a hydroxyl group in molecular chain terminals was obtained. The number average molecular weight of this thing was 2350, and, as for 0.94 meq/g and viscosity, 431 poise/30 \*\*, and the bromine number of hydroxyl group contents were 1g/100g. The number of average hydroxyl groups per molecule at this time is 2.21.

[0063]The raw material except a polyisocyanate compound was blended among the constituents shown in Examples 1-7 and the comparative example 1 – the 5 1st table, mixed stirring was carried out at 60 \*\* for 2 hours, and the compound of the liquefied polymer was obtained. In addition, mixed stirring was carried out for 2 minutes at 60 \*\* with a rate which shows a polyisocyanate compound in the 1st table at this, and the liquefied polymer composition was obtained. This was passed on a 300x150x2-mm metallic mold, curing after accelerated hardening was carried out at 60 \*\* after a 2-hour press at 60 \*\* for 15 hours, and the cured body was obtained. The evaluation result using this cured body is shown in the 1st table.

[0064]Evaluation of the heat resistance of a cured body and workability was performed by the following methods.

(1) The cured body produced by carrying out was heated for 150 \*\* x one week in gear type oven like the heat resistance test above. The physical properties after heating were measured based on JIK K 6301. It was shown in the 1st table by making the rate of a weight change from an initial mass into loss on heating.

[0065](2) the workability profit \*\*\*\* liquefied polymer composition was put into a 500-ml glass

bottle, and viscosity was measured with the B8M mold viscosity meter (No.4 rotor) after maintenance for 1 minute at 25 \*\* in the constant temperature bath. From the obtained viscosity result, it evaluated in accordance with the following standard.

O; -- viscosity -- less than [ 50 poise ] \*\*; -- viscosity -- less than [ 50 poise or more 100 poise ] x; -- it becomes difficult for the viscosity of a compound to operate defoaming operation, casting and to be impregnated, spreading, etc. at 100 poise or more to general 100 poise or more in viscosity.

[0066]

[Table 1]

|                             |                           | 実施例  |      |      |       |       |      | 比較例  |      |      |       |      |      |
|-----------------------------|---------------------------|------|------|------|-------|-------|------|------|------|------|-------|------|------|
|                             |                           | 1    | 2    | 3    | 4     | 5     | 6    | 7    | 1    | 2    | 3     | 4    | 5    |
| 液状ジエン<br>系重合体の<br>水素化物<br>組 | 製造例 1                     | 100  | —    | —    | 100   | 100   | 100  | 100  | —    | —    | —     | 100  | 100  |
|                             | 製造例 2                     | —    | 100  | —    | —     | —     | —    | —    | —    | —    | —     | —    | —    |
|                             | 製造例 3                     | —    | —    | 100  | —     | —     | —    | —    | —    | —    | —     | —    | —    |
| 反応性<br>希<br>成<br>可塑剂        | KX-501                    | 11   | 51.9 | 85.0 | 51.9  | —     | —    | 51.9 | 64.9 | —    | 51.9  | —    | 51.9 |
|                             | ポリテールHA                   | 23   | —    | —    | 202.2 | —     | —    | —    | —    | —    | —     | —    | —    |
|                             | GI-1000                   | 33   | —    | —    | —     | 145.7 | —    | —    | —    | —    | 145.7 | —    | —    |
| 硬化触媒<br>成                   | 出光PAO 5010                | 44   | 100  | 100  | 100   | 130   | 130  | 100  | 30   | 100  | 100   | 130  | —    |
|                             | DBTDL                     | 55   | 0.2  | 0.2  | 0.2   | 0.2   | 0.2  | 0.2  | 0.2  | 0.1  | 0.2   | 0.2  | 0.1  |
| 老化防止剤<br>物                  | イルガノックス1076 <sup>6)</sup> | 0.5  | 0.5  | 0.5  | 0.5   | 0.5   | 0.5  | 0.5  | 0.5  | 0.5  | 0.5   | 0.5  | 0.5  |
|                             | デスマジュールW                  | 73   | 42.8 | 70.1 | 42.8  | 42.8  | 42.8 | 50.0 | 14.3 | 28.6 | 28.6  | 42.8 | 14.3 |
| 硬化剤<br>物                    | ミリオネートMTL <sup>8)</sup>   | —    | —    | —    | —     | —     | —    | 47.3 | —    | —    | —     | —    | —    |
|                             | OH (B) / OH (A)           | 9)   | 2.0  | 2.0  | 2.0   | 2.0   | 2.0  | 2.0  | 2.5  | —    | 2.0   | 2.0  | —    |
|                             | NCO / OH                  | 1.15 | 1.15 | 1.15 | 1.15  | 1.15  | 1.15 | 1.15 | 1.15 | 1.15 | 1.15  | 1.15 | 1.15 |
| コントロール<br>耐<br>価            | 硬さ JIS A                  | 37   | 44   | 38   | 30    | 29    | 43   | 47   | 32   | 72   | シート   | 49   | 26   |
|                             | 硬さ JIS A                  | 35   | 42   | 36   | 26    | 25    | 40   | 44   | 10   | 69   | 化粧    | 48   | 試験片  |
|                             | 加熱減量 %                    | -0.7 | -0.6 | -0.5 | -1.0  | -1.0  | -0.7 | -0.5 | -1.1 | -0.5 | —     | -0.5 | 溶融   |
| 作業性                         | 性                         | ○    | ○    | ○    | ○     | ○     | ○    | △    | ×    | ○    | ○     | ○    | ○    |

[0067][The footnote of the 1st table]

1); Dimer diol KX-501 (made by Arakawa Chemical Industries, Ltd.), the mixture of the weight ratio 133 to 8 of saturated dihydric alcohol of the carbon number 36, and saturated dihydric alcohol of the carbon number 72, Hydroxyl group content =3.62 meq/g2; The hydride of hydroxyl group content liquefied 1,2-polybutadiene (product made from Mitsubishi Kasei Industry), Hydroxyl group content = 0.93 meq/g, Mn=2180, and 1,2 combination The hydride of 91%3; hydroxyl group content liquefied 1,2-polybutadiene (made by Nippon Soda Co., Ltd.), Hydroxyl group content = 1.29 meq/g, Mn=1400, 1, and 2 combination is content =98.1 wt %5; dibutyltin dilaurate (product made from Common Medicine) of 93%4;1-decene oligomer (product made from Idemitsu Petrochemistry), kinetic viscosity =70.3cst (37.8 \*\*), 4 and 5, and a hexamer.

6); hindered phenolic antioxidant (made by Ciba-Geigy Japan)

7) the; hydrogenation MDI (product made from Sumitomo Beyer Urethane Industry), isocyanate content =31.8%8; The liquefaction degeneration MDI which uses diphenylmethane diisocyanate as the main ingredients (product made from Japanese Polyurethane Industry). Isocyanate content =28.8%9; the number of hydroxyl group mols in the hydride in reactive diluent of the number of hydroxyl group mols / hydroxyl group content liquefied diene system polymer of (B) (A) [0068] [Effect of the Invention]According to this invention, the liquefied polymer composition which was excellent in workability by hypoviscosity is obtained. And the hot heat resistance of the cured body produced by carrying out curing treatment of this constituent is good, and it is low hardness (50 or less JIS A). Therefore, this invention can be effectively used as an electric insulation material, a coating material, a paint, a water blocking material, a protective layer, etc.

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[Translation done.]